ACID-SULFATE WEATHERING OF SYNTHETIC MARTIAN BASALT: THE ACID FOG MODEL REVISITED. N. J. Tosca, S. M. McLennan, D. H. Lindsley and M. A. A. Schoonen, Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 (Nick@pbisotopes.ess.sunysb.edu)

Introduction: One of several models that has been proposed to explain the present chemical and mineralogical nature of the Martian surface is referred to as the "acid-fog" model. This model involves the recent (up to 1Ga), slow and continuous interaction of acidic volatiles, presumably of volcanic origin, with the exposed Martian basaltic crust [1, 2]. As a result of this interaction, mineral dissolution occurs and subsequent evaporation of the fluid results in formation of evaporite salts. Banin et al. [2] have tested the acid-fog model experimentally by interacting terrestrial analog basalt with sulfuric, hydrochloric and nitric acid mixtures and found that upon fluid evaporation, the Ca and Al-sulfate salts gypsum and alunogen precipitated as secondary mineral phases with no other phases detected by X-ray diffraction.

The study presented here revisits this model using more relevant Martian basaltic analogs synthesized in the laboratory. Results show that the chemical and mineralogical composition of the basaltic analog material is critical in determining fluid chemistry and the subsequent secondary products that are formed. Different chemical compositions of basaltic analogs are used in this study to provide a thorough evaluation of fluid-rock interaction as a function of host rock composition.

Experimental and Analytical Procedures: The compositions of synthetic basaltic analogs used in this study include those most relevant to one of the most important sources of chemical data for the Martian surface - the Mars Pathfinder landing site. As an attempt to encompass the chemical spectrum that the Pathfinder data may reflect, two "end member" compositions are used as analogs. These compositions include a low-S Pathfinder rock composition representative of a basaltic andesite Pathfinder surface rock composition and averaged Martian soil (recalculated on a S- and Cl-free basis), which may represent a typical upper crustal composition.

The basaltic analog materials are synthesized following the procedure outlined by Tosca et al. [3] to achieve the desired compositions. The products are then lightly crushed and sieved to constrain the particle size between 700 and 70 μm. The analog material is then ultrasonically rinsed in acetone to remove ultrafine particles and dried overnight at 120 °C. The dried material is then divided and added to 5 different sulfuric/hydrochloric acid mixtures with a S:Cl molar ratio of 4, equal to that observed in the Pathfinder soils. Acid mixture concentrations range from a 1M H_2SO_4/0.25M HCl mix to 100μM H_2SO_4/25μM HCl, each decreasing in concentration by a factor of 10. The fluid-rock mix is then enclosed in a Teflon® beaker kept at 25 °C and allowed to react for a period of 14 days, periodically being opened to retain equilibration with the atmosphere. After the 14-day reaction period, beakers are dried carefully at 45-55 °C for 2 days to prevent any volatilization of H_2SO_4 or HCl [2]. In order to investigate the effect of varying the crystallinity of the starting material, experiments are conducted with pure basaltic glass as well as an almost entirely crystalline (4-5% interstitial glass) basalt. In addition, fluid-rock ratios of 1 and 10 are used for each acid concentration and crystallinity to investigate potentially important aqueous chemical processes.

The analytical procedures utilized throughout the course of these experiments include initial material characterization by electron microprobe, X-ray diffraction (XRD) and infrared spectroscopy (FT-IR). In-situ aqueous analysis is limited to experiments with a fluid-rock ratio of 10, a result of the small amount of material produced by synthesis (approx. 300 mg per beaker) and thus, the small amount of fluid used. Experiments are sampled over the course of the 14-day period for analysis by atomic emission spectroscopy (DCP-AES) so that the fluid removed does not exceed 4% of the total. Final material characterization includes XRD, FT-IR and scanning electron microscopy (SEM), which also permits energy dispersive X-ray microanalysis (EDS) for secondary mineral identification.

Results: During the 14-day reaction period, various dissolution processes of the glass and major minerals of the basalt largely control the fluid chemistry. Consequently, upon fluid evaporation, the saturation state of various minerals in the fluid determines the precipitation sequence of secondary phases. Although precipitation of several secondary phases may be thermodynamically favorable, there are a variety of kinetic factors that appear to control the mineral dissolution, fluid chemical and precipitation processes. As a result, many important secondary phases are observed to precipitate as poorly-crystalline minerals. Detection of such poorly-crystalline phases is important in that the poorly-crystalline nature of Martian soils has been proposed in light of various spectroscopic data from the surface of Mars [4]. These phases are detected by SEM, which gives chemical as well as morphological information.

In experiments using acid mixtures of high concentrations (1M H_2SO_4/0.25M HCl and 0.1M H_2SO_4/0.025M HCl mixes), dissolution proceeds stoichiometrically with chemical constituents being released in their bulk proportions. Aqueous Fe/Ti ratios suggest that large amounts of Fe^{2+} and Fe^{3+} are released in solution from the stoichiometric dissolution of small amounts of Fe-Ti oxides present in the basalt.

In experiments using lower-concentration acid mixtures (10mM H_2SO_4/2.5mM HCl to 100μM H_2SO_4/25μM HCl mixes), dissolution proceeds non-stoichiometrically. This non-stoichiometric dissolution preferentially releases cations bound in crystal sites with higher Madelung site energies. Higher Madelung site energy, or the work required to bring an ion into a site from an infinite distance, is indicative of weaker bonding [5]. Results from these experiments show that in pyroxenes, cations occupying higher Madelung energy M2 sites are released into solution faster and in higher amounts than those occupying lower energy M1 sites. As a consequence, pyroxene dissolution forms a M2 cation-depleted, porous surface layer rich in structural silica and, to a lesser degree, rich in M1 cations. SEM analyses of reacted pyroxenes provide some evidence of such layers, but more importantly, show that pyroxenes containing Fe dissolved under oxic conditions form an insoluble Fe-oxyhydroxide surface layer in addition to a silica rich layer which may also retard further mineral dissolution. These results are consistent with several other dissolution studies of individual pyroxenes [6]. A similar process has been observed with plagioclase preferentially releasing alkali and alkaline earth cations, as well as for basaltic glass releasing univalent and divalent network modifying cations.

The evolution of the fluid chemistry in these experiments begins with weakly-bound cations being released into solution, which raises the fluid pH. In high acid concentrations, the flux of cations into solution is much larger which creates solutions similar to acidic brines, with sulfate minerals precipitating from solution. With low acid concentrations, the increase in pH is much more drastic and causes a large increase in Fe^{2+} oxidation rate and formation of poorly-crystalline and in some cases, abundant secondary iron oxide phases.

The fluid-rock ratio in these experiments is an important factor in determining several fluid chemical processes. For example, Fe^{2+} oxidation does not proceed as far in low fluid-rock ratios due to lower dissolved Fe^{2+} and O_2 content in the bulk fluid. This also has an effect on the abundance and crystallinity of precipitated phases due to a lower level of dissolved solids.

The formation of evaporite salts should be largely dependent on the saturation state of those minerals in the fluid. However, the lack of well-crystalline phases during glass dissolution as compared to mineral dissolution indicates that precipitation may also be controlled by a number of surface characteristics such as the density of defect sites available for nucleation. The well-crystalline evaporite salts found in these experiments include gypsum and two morphologically different Fe-sulfate phases. Also, in experiments where appreciable amounts of silica have been released into solution, small amounts of amorphous silica have been detected.

Implications for the Acid Fog model: The results presented here show that fluid-rock interaction is largely dependent on the chemical and mineralogical properties of the material being altered by surficial processes. The main differences in chemical compositions of the starting materials used in this study opposed to [2], such as higher Fe content, lower Al content and presence of pyroxenes, result in distinctly different secondary phases. The detection of secondary Fe-oxides and oxyhydroxides, both as coatings and individual grains, imply that ferric phases may be an important product during this process. The content and crystal sites of Fe in the starting material are thus crucial in determining possible origin of ferric phases on the surface of Mars. Also, the detection of phases that have been proposed by other studies such as amorphous silica [7], Fe-sulfates and other salts [8, 9] suggests that synthetic analogs may be more relevant in testing models of Martian soil formation. The presence of several poorly-crystalline alteration phases resulting from these experiments agrees with numerous studies that have suggested the same for the nature of the Martian soil [4, 10]. The nature of fluid-rock interactions are complex and many thermodynamic and kinetic factors play an important role in determining fluid chemistry as well as the precipitation of secondary phases. Therefore, when experimentally testing models of surficial processes on Mars, a relevant analog material is essential in determining the validity of such models.

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